

2. LITERATURE REVIEW

Currently, world energy production is dominated by all types of fossil carbon fuels. This has caused and will continue to cause great and growing concern for the global environment. As Fyfe and Powell (1991) listed, these concerns include: (1) the accelerating increase in global greenhouse gases (CO_2 , CH_4 , CFC's); (2) the depletion of the ozone (O_3) layer, increased ground levels of ultraviolet radiation, acid rain; (3) reduction in biodiversity; (4) pollution from all forms of waste products; (5) the catastrophic state of social imbalance. Present trends in the use of fossil carbon fuels are not sustainable and the potential amount of atmospheric pollution will almost certainly have intolerable consequences.

Combustion of coal produces a variety of residues including fly ash and bottom ash. Fly ash is the residue from coal combustion that enters the flue gas stream. It is composed predominantly of fine particles and is either collected in emission control devices, such as electrostatic precipitators, mechanical filters, or released from the stack. Fly ash contains all naturally occurring elements and is substantially enriched in trace elements compared with the parent coal (Adriano *et al.*, 1980).

Particulates emitted into the atmosphere are potentially hazardous due to their influence on human and animal health. Despite their relatively small quantities, they are consist of micron- and submicron- sized particles and as such, are readily inhaled and may have far reaching effects on human health. Collected residues may also eventually adversely effect the environment since it is expected that huge amounts will have to be disposed of on land.

2.1. Microscopic features of fly ash

The most typical microscopic feature of fly ash revealed by scanning electron microscopy of particles less than 53 μm are shown in Figure 2.1. As seen in this figure, the fly ash matrix is composed predominantly of spherical particles of various sizes. Large-sized spheres have thick walls and are hollow. Small-sized spheres are contained in the wall cavities of larger spheres, attached to their surfaces, or enclosed within their structure (Page *et al.*, 1979). Figure 2.1.d shows evidence of submicron ash particles. Figure 2.1 also shows that particles of fly ash, regardless of their size, have a strong tendency for aggregation, this property makes it difficult to assess the effective particle diameters of fly ash, since clusters of particles seem to be continuously forming. Fly ash particle size and shape are in relation to precipitation efficiency in power generation plants. The larger the particle fraction ($>5\ \mu\text{m}$ in diameter) and the more spherical the particle is, the greater the precipitation efficiency of the electrostatic precipitator and hence, the lesser the amount of fly ash particulates available for atmospheric emission.

2.2. Trace elements content in fly ash

In India, a large project to study the trace elements content of coal and coal by products from several large coal fields was conducted. Significant abundance of trace elements have been observed in the coal bearing horizons of the Godavari Valley coal belt (Pavanaguru *et al.*, 1991). Data from samples collected at this area indicated significant variation in the vertical distribution of trace elements and partitioning between high and low ash samples. Analysis of feed coals and fly ash also indicated enrichment of as much as 10 times in some trace elements in fly ash relative to the coal (Powell *et al.*, 1991, Sahu, 1991). It can be explained that coal deposits are repository of many toxic metals volatilize at furnace temperature but down stream the ash dust the fall of temperature enable their condensation in the ash matrix. Studies have shown that many trace elements in the fly ash are concentrated in the smaller ash particle size. Among the elements generally enriched in the ashes are As, B, Ca, Mo, Se, S, and Sr.

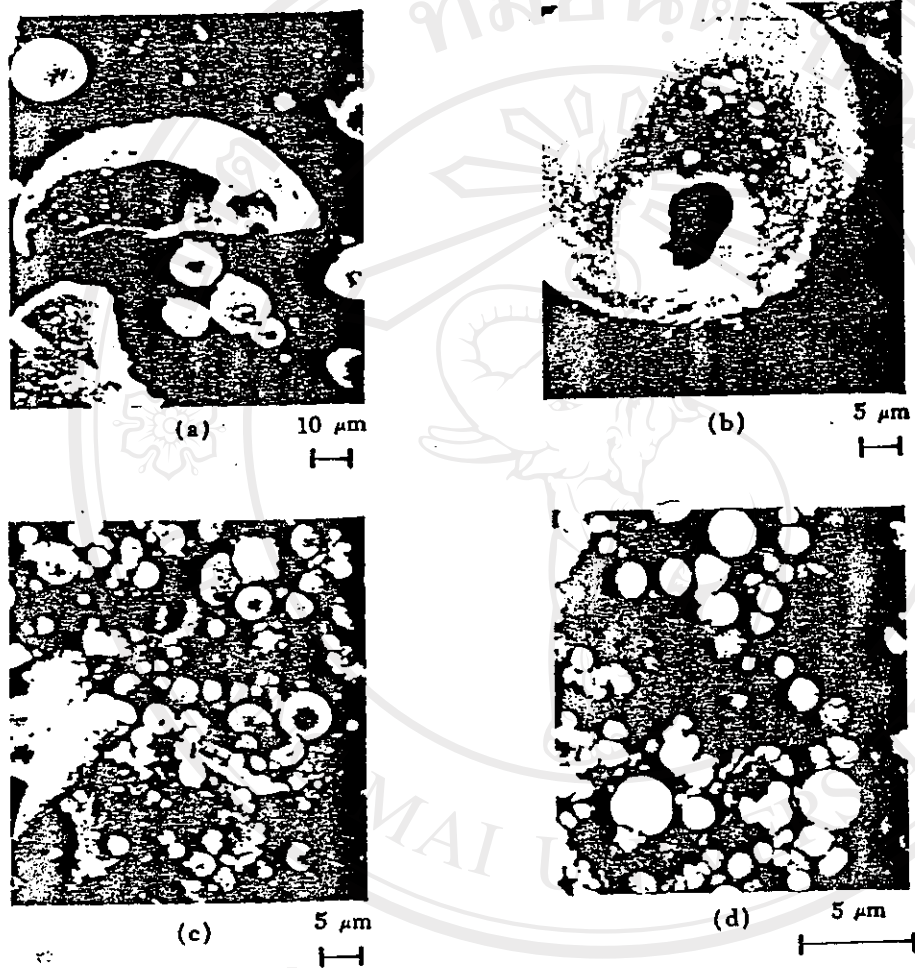


Figure 2.1 Electron micrographs of fly ash particles of different size

Source : Page *et al.*, (1979)

In a chemical analysis of Mae Moh lignite ash by using Auger Electron Spectroscopy (AES), X-ray Photoelectron Spectroscopy (XPS), Secondary Ion Mass Spectroscopy (SIMS) and X-ray fluorescence (XRF), Ratanasthien *et al.* (1991) revealed that the elements of Al, Ca, Fe, Mg, K, Na, Si and Ti were above 0.1 percent; the elements above 100 ppm were As, Ba, Mn, Rb, Sr and V and the elements found in significant amount but below 100 ppm were Ce, Co, Cr, Cs, Dy, Hf, La, Mo, Mo, Ni, U, Sb, Sc, Ta, Tb and Th. The highest concentrations of the elements As, Co, Cr, Ni and U are found in the finest fly ash particles analyzed (Table 2.1)

Table 2.1. Concentration of some elements in coal, fly and bottom ash from Mae Moh Power Plant

Element	Coal ^a	Fly Ash ^b	Bottom Ash ^b
As (ppm)	45.45	213	18.3
Co (ppm)	9.53	33.7	32.8
Cr (ppm)	23.01	66.5	63.7
Fe (%)	3.01	11.01	8.04
Mo (ppm)	3.34	19.9	11.2
Ni (ppm)	27.61	53.3	52.1
Th (ppm)	3.48	17.1	16.9
U (ppm)	1.94	6.21	5.57

^a : Fyfe *et al.*, 1993

^b : Ratanasthien *et al.*, 1991

Coal fly ash from 22 Indian power plants collected and analyzed by Negi and Meenakshy (1991) using Energy Dispersive X-ray fluorescence (EDXRF) and Instrumental Neutron Activation Analysis (INAA) methods. The Authors concluded that the concentration of trace elements were 1.5 to 3 times higher in lignite ash as compared to coal ash. There was inter element correlations in the fly ash samples of Ti with Fe, Si with K and Cu, Zn with Pb, K with Rb and Ca with Sr.

Also, the concentration of some elements like Ce, Co, Cr, Cu, Hf, Pb and Rb was found to be higher in smaller size particles as compared to large ones.

Bauer and Andren (1988) study variability of particulate trace element emission from Columbia coal-fired power plant in Portage, Wisconsin. Parameters evaluated for both total particles and 16 individual elements included volume concentrations, mass emission rates, enrichment factors, and size distributions. In general, variations over several weeks or more were much larger than those within a given day. Small particles were strongly enriched in As, Ba, Br, Cr, Se, Sb and Zn. Concentration of individual elements varied by as much as 10 times at a given particle size. The authors also found that the two combustion units were generally similar in behavior, although the newer unit often emitted a factor of 3 less particulate mass with somewhat smaller particle size.

To assess the potential of environmental pollution by coal of Pathakhera Coal Field, India, Nandgaonkar (1991) took samples of fly ash and bottom ash and analyzed them to compare the data. The results showed that toxic elements such as Fe, Al, Mn, Cd, Co, Cu, Hg, Ni, Pb, Zn and Zr were released into the ecosystems of the waste disposal area; but their effect, potential pollution, as well as power and dispersion patterns in the ecosystem is not yet completely understood. While generating 1150 MW of electric power, a thermal power plant situated within the vicinity of the coal field discharges about 1 million tones of particulate ash as waste in ash ponds. Particulate and gaseous products emitted from stacks of coal-fired power plants eventually are deposited on land and in aquatic ecosystems. Trace elements from coal combustion may enrich the surrounding environment.

2.3. Trace elements enrichment of soil around power plants

Fly ash concentration ranges for As, Cd, Hg, Pb, Se and Zn are sometimes greater than soil by a factor of 100 or more. Presumably, the fly ash escaping from such power plants would be further enriched in the surrounding environment. In recent years several studies have assessed the magnitude of atmospheric trace elements deposition from power plants. The study of Klein and Russell (1973) reported that vegetation and soil near a Michigan power plant (USA) contained elevated levels of Cd, Cr, Cu, Hg, Co, Ni, and Zn. Several volatile elements in coal pose a potential hazard to the environment, but there is little evidence for any marked accumulation in soil around power plants. Some studies detected no impact of power plant emission on trace element levels in the surrounding environment. Serious environmental contamination from power plants is apparently confined to those facilities burning coal with unusually high trace element concentrations. Emissions of As from coal combustion rival the total natural emission rate for this report are released in significant amounts, the contribution to the total anthropogenic flux appears to be relatively small, with the exception of Hg.

To determine the influence of technical and operational changes in electric power generation on the deposition of water-insoluble particulates in the agricultural environment surrounding the power plant and determining the amounts and concentration of Cu, Mn, Zn, Ni, and Pb in the particulate matter being deposited during the summer months near Chalk Point, Mastradone *et al.*, (1982) collected dustfall deposition during summer for four years and analyzed the trace elements. The authors found the reduction in particulate deposition rate coincided with 37% reduction in power generation output from two 330MW coal-fired units and the onset of 660MW oil-fired generation unit. Prior to the oil-fired unit operation, the rates of Cu, Mn, and Pb deposition was significantly higher in the site nearby, but the rates were significantly

reduced and showed no relationships to distance or direction from the source after the new unit began operating.

Field studies to monitor power plant emissions utilize a general concept in which evidence of continuation is suggested where concentrations of a particular element in soil or vegetation in regions surrounding the emission source are inversely related to the distance from the source. Various attempts have been made to model ground level, surface-air concentrations of particulates emitted from coal-fired power plants. Vaughan *et al.*, (1975) used a source-depletion model applied to 1400MW power plant in the St. Louis, Missouri area, USA (Figure 2.1a). Mass deposition rates computed from air concentration shows that deposition decreases as a function of distance from the source. Lyon (1977) developed a model for particulate emission and deposition derived from their data which is presented in Figure 2.1b. Soil enrichment was calculated, but the findings indicated that the probability of observing and enrichment would be even slighter.

Based upon a maximum deposition rate of 50 kg/ km^2 , Page *et al.* (1979) estimated soil enrichment of trace elements for a 3000MW coal-fired power plant with an assuming 35 year lifetime (Table 2.2). From this table, it is shown that soil enrichment, except for Se, appears negligible over the 35 year exposure period. Thus, trace element enrichment in soil from particulate emission of coal combustion predicted by models developed for diverse conditions seems quite low and, in many cases, not measurable by current technology.

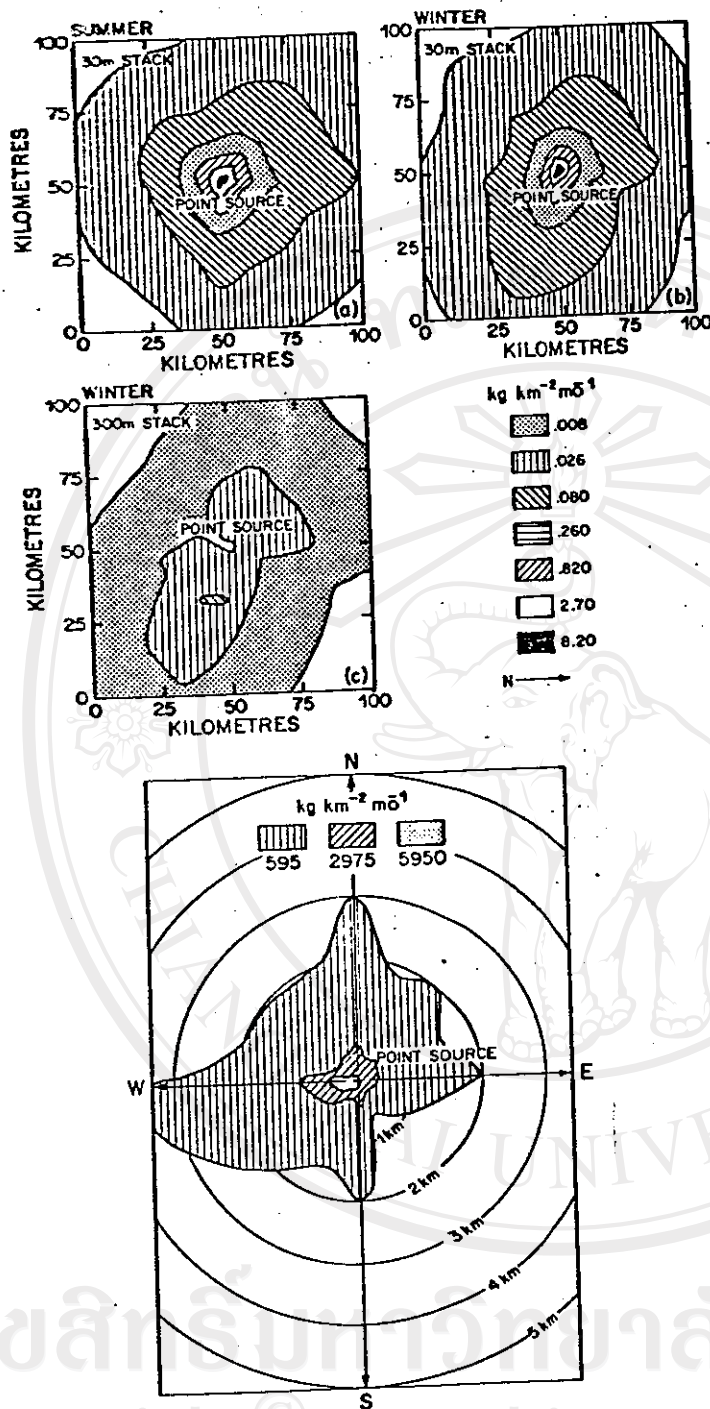


Figure 2.2.. Modeled mass deposition of fly ash around power plants

a: 1400-MW coal-fired power plant in the St. Missouri area

b: 870-MW coal-fired power plant in Memphis, Tennessee

Emission rate = 1g/s ; deposition velocity = 1 cm/s

Particle size $<15\text{ }\mu\text{m}$

Source: Elseewi *et al.*, (1986)

Table 2.2. Estimated maximum deposition of trace elements onto soil adjacent to a coal-fired power plant

Element	Amount Deposited (mg/kg)		Common Concentration (mg/kg)		Soil enrichment (%)
	Annual	Lifetime ^a	Typical	Range	
As	0.00039	0.014	6	0.1-40	0.2
Cd	0.000014	0.0005	0.006	0.01-7	0.8
Pb	0.00082	0.029	15	2-200	0.2
Mo	0.00015	0.0052	2	0.2-5	0.3
Se	0.00059	0.021	0.2	0.01-2	10.5
U	0.000087	0.003	1	0.1-10	0.3
Zn	0.00163	0.057	50	10-300	0.1
Sb	0.000061	0.0021	6	2-10	0.04
Be	0.00003	0.0011	6	0.1-40	0.02
Cr	0.00019	0.0066	100	5-3000	0.007
Co	0.000062	0.0022	8	1-40	0.03
Cu	0.00041	0.0144	20	2-100	0.07
Ga	0.00053	0.0182	30	0.4-300	0.06
Ni	0.00012	0.0042	40	10-1000	0.01
Th	0.0009	0.0032	5	0.1-12	0.06
V	0.00097	0.034	100	20-500	0.03

^a : assuming 35 year lifetime

Source: Elseewi *et al.*, 1986.

Sato Kazuo and Sada Koichi (1992) in Japan evaluated increases in trace element (As, Cd, Cr, Cu, and Hg) concentrations in surface soils caused by deposition of emissions from a power plant through field studies and model calculations. The enrichment discrimination factor (EDF) was used as an indication of the effects of this deposition. Model calculations estimated that the maximum deposition of these elements would be located at a site 3 km north of the plant. The increase in EDF, Delta E, at the site due to cumulative depositions over 25 years was evaluated to be As : 0.06, Cd:0.20, Cr: 0.02, Cu : 0.13 and Hg : 0.08, respectively. In contracts, observed EDFs of each element at 30 sites within a 10 km radius from the plant fluctuated within the range far

beyond the Delta E, and there was no statistically significant correlation among the EDFs as a function of distance or direction from the plant, suggesting that the effects of emissions lie concealed in normal ambient fluctuation of the element concentrations .

2.4. Effect on soil pH

Coal combustion products, in contact with water produce solutions which are generally alkaline. When mixed with soils, alkaline fly ash induces an increase in the soil pH which is dependent upon the buffering capacity of the recipient soil, the amount of fly ash added, and the time of contact. Calcareous soil, which is dominant in the arid and semiarid southwestern USA, are highly buffered compared with acid soil. They show an initial increase in their pH upon coal ash addition, which diminished with time to levels comparable to background values (Page *et al.*, 1979. Elseewi *et al.*, 1978). However, the effects of small atmospherically dispersed solid particles from coal combustion sources on soil pH have not been investigated. Prince and Rose (1972) noted that rain in East Germany downwind from power plants burning lignite was alkaline, presumably from washout of basic particulate. Primary oxides of S and N which have been implicated in acid rain formation induce an effect on soil pH opposite to that observed for small solid particles.

2.5. Effects of ash disposal on terrestrial ecosystems.

The major potential adverse impacts of ash disposal on terrestrial ecosystems include leaching of potentially toxic substances from the ash into soils and ground water, reductions in plant establishment and growth on the ash, changes in plant elemental composition, and increased cycling of potentially toxic elements through the food chain. (Carls and Adriano, 1993; Elseewi *et al.*, 1986). Collected residues may also eventually adversely effect the environment since it is expected that huge amounts will have to be disposed of on land. Land disposal of these residues may mobilize their

beneficial and/or hazardous constituents, thereby affecting, to varying degrees, the quality of surface and ground waters, soils, and vegetation which in turn affect accumulation of these constituents by animals and man.

2.5.1. Effects on surface and groundwater

Information available from field studies indicates that the actual effects of ash disposal on groundwater quality largely depend on the physical and chemical characteristics of the ash and the hydrogeologic characteristics and climate of the disposal site. As Sharma (1991) reported, a high concentration of arsenic, chromium, lead, nickel and cadmium in water samples around Barauni (India) is a direct consequence of fly ash discharge into the Ganga River.

2.5.2 Effects on Vegetation

Establishment of vegetation on ash disposal sites serve a variety of functions, including stabilizing the ash against wind and water erosion, providing shelter and habitat for wildlife, and providing a more aesthetically pleasing landscape. However, reclamation of these sites often proceeds slowly due to the presence of physical and/or chemical conditions in the ash that are deleterious to plant survival and growth. The major factors limiting vegetation establishment on ash disposal sites are: lack of essential nutrients, toxicity caused by high pH and/or high soluble salt concentrations, high concentrations of other potentially toxic trace elements, and the presence of compacted and/or cemented layers in the ash. Plants growing on ash basin generally accumulate elevated levels of trace elements enriched in the ash. These elements may include As, B, Co, Cr, Cu, Hg, Mo, Ni, Pb, Se, and Zn (Elseewi et al., 1981; Carlson and Adriano, 1991; Elseewi and Page, 1984). From these studies, it is evident that ash deposits covered with a soil cap influence plant elemental

concentration. Table 2.3 shows estimated trace element contamination of vegetation arising from emissions from a coal fired power plant.

More investigations carried out in the United States have demonstrated positive growth response for a number of crop species to incorporation of small to moderate amounts of fly ash in agricultural soil. The increase of yield was as results of increased availability of some elements such as Zn, Mo, S and attributed to water availability to plants. Greenhouse experiments conducted with fly ash from a western United States coal source (Mohave fly ash) added to a desert calcareous and three acid soils in rates ranging up to eight per cent by weight have demonstrated improved yields of a number of crop species.

Table 2.3. Estimated trace element contamination of vegetation arising from emission from a coal-fired power plant

Element	Conc in/on vegetation (μg element/g dry matter)	Typical concentration (μg element/g dry matter)
As	0.07	0.4
Cd	0.002	0.2
Cr	0.034	1.5
Cu	0.074	10
Pb	0.15	3
Mo	0.027	1
Se	0.107	0.2
Zn	0.30	25
Sb	0.011	0.06
Be	0.006	0.03
Co	0.011	<1.0
Ga	0.096	1.2
Ni	0.021	5
Th	0.016	0.05
U	0.016	0.04
V	0.18	1

Source: Page *et al.*, 1979

2.5.3 Food chain effects

Selected analysis of Mo in various plant species grown on calcareous and acid soils supplemented with fly ash showed that concentrations of Mo in alfalfa and white clover reached as high as 22.0 and 44.4 $\mu\text{g Mo/g (ppm)}$, respectively. Analysis also showed that Sr, Ba, Se, Co and Cs exhibited definite concentration trends in plant tissue with increasing rates of fly ash application to soil of up to eight percent by weight. The increase in Sr and Ba concentrations indicated that these two elements could serve as an index of fly ash deposition on soils and vegetation in area adjacent to coal-fired power plants in western United States. Increases in concentrations of Se and Mo suggested potential animal nutritional problems when forage crops are grown on fly ash-amended soils (Page *et al*, 1979). Because plants growing on fly ash frequently accumulate elevated levels of plants selenium, it is important to determine the potential impact on animals consuming these food. Selenium present in the ash was readily accumulated by plants and then transferred up the food chain to animals consuming the plants, resulting in increased accumulation of selenium in animal tissues. This could be beneficial in areas where selenium deficiency is a problem. However, because of the narrow range between deficient and toxic levels of selenium in animal diets, selenium levels in plants growing on ash basins and the animals consuming them should be monitored closely.

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